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KAWAMOTO, Tomohiro et al.
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For: Piezoelectric Ceramic and Laminated Piezoelectric Element

VERIFICATION OF TRANSLATION

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Date: May 10, 2006

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Keiji Tokieda

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(Title of the Invention)
Piezoelectric Ceramic and Laminated Piezoelectric
Element
(Technical Field)
The present invention relates to a piezoelectric
ceramic and, more specifically, to a piezoelectric
ceramic suited for a laminated piezoelectric actuator,
a piezoelectric transformer and an ink-jet printer
head.
(Background Art)
A co-fired laminated piezoelectric element having
internal electrodes has heretofore been known, and has
been applied to a laminated piezoelectric actuator, a
piezoelectric transformer and an ink-jet printer head.
The co-fired laminated piezoelectric element is
fabricated by co-firing a laminate obtained by
alternately laminating ceramic green sheets (that
serve as piezoelectric layers) and conducting patterns
(that serve as internal electrode layers), and by
forming external electrodes thereon, and produces a
predetermined displacement by utilizing a counter-
piezoelectric effect possessed by the piezoelectric
material.
As the piezoelectric ceramic that constitutes
piezoelectric layers of the laminated piezoelectric
element, there has been widely used a perovskite
composite oxide having an ABO_3 composition. For
example, JP-A-2002-293625 (prior art (a)) discloses a
piezoelectric ceramic comprising a perovskite
composite oxide containing Pb as an A-site element,
and Zr and Ti as B-site elements, wherein the A-site
element (Pb) is partly substituted with Ca, Sr and Ba,
the B-site elements (Zr, Ti) are partly substituted
with a rare earth element such as Dy and by W, and the
A/B site ratio is set to be 0.955 to 0.99, in an

attempt to improve a piezoelectric distortion constant and a Curie point. Further, JP-A-2002-299710 (prior art (b)) discloses a piezoelectric ceramic comprising a perovskite composite oxide wherein the B-site elements (Zr, Ti) are partly substituted with W, Zn and Nb, enabling the firing to be conducted at a low temperature due to being substituted with Zn and Nb, and, further, making it possible to co-fire the internal electrodes having an Ag ratio of not smaller than 90% by mass.

The piezoelectric ceramics disclosed in the above prior arts (a) and (b) are fabricated by, first, weighing the starting powders of PbO, ZrO_2 and TiO_2 in predetermined amounts, wet-mixing these powders by using a ball mill or the like, drying the mixture, calcining the mixture under a predetermined temperature condition, milling the calcined body again by using the ball mill or the like to obtain a desired grain size distribution, forming a desired molded body by using a slurry obtained by adding an organic binder or an organic solvent to the powder of the calcined body, and firing the molded body.

However, the piezoelectric ceramic disclosed in the prior art (a) must be fired at a temperature of as very high as 1150°C to enhance the piezoelectric characteristics, making it difficult to conduct the firing at a temperature of as low as, for example, 1000°C or lower. That is, when the firing is conducted at a temperature of 1000°C or lower, the Curie point and the piezoelectric distortion constant become so low that desired piezoelectric displacement characteristics are not obtained. Further, a high firing temperature makes it difficult to co-fire the internal electrode layers in combination with the piezoelectric ceramic, which is disadvantageous from

the standpoint of lowering the cost.

The piezoelectric ceramic disclosed in the prior art (b) which contains sub-components such as Zn and Nb, can be co-fired together with the internal
5   electrode layers that contain not less than 90% by mass of Ag causing, however, the Curie temperature to decrease with an increase in the amount of addition of Zn and Nb. Therefore, the thus obtained laminated piezoelectric element is accompanied by a problem of
10   low durability and low reliability against high temperatures.

As described above, none of the conventional piezoelectric ceramics simultaneously satisfy the assignments of high piezoelectric characteristics and
15   firing at a low temperature.
(Disclosure of the Invention)

It is, therefore, an object of the present invention to provide a piezoelectric ceramic that can be fired at a low temperature, has a high Curie
20   temperature and a high piezoelectric distortion constant, as well as excellent durability and reliability against high temperatures.
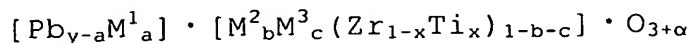
Another object of the present invention is to provide a method of producing a piezoelectric ceramic
25   having the above-mentioned characteristics and a laminated piezoelectric element using the above piezoelectric ceramic.

According to the present invention, there is provided a piezoelectric ceramic comprising a
30   perovskite composite oxide of an ABO_3 composition containing Pb in the A-site and Zr and Ti in the B-site, wherein when the total amount of the element species constituting the B-site of the perovskite composite oxide in the ceramic is set to be one mol,
35   an average valency of the element species constituting

the B-site is in a range of from 4.002 to 4.009.

In the present invention, the average valency of element species constituting the B-site is found as described below (the valency stands for a value of ionization stemming from a general balance of electrons of elements in the periodic table). For example, when there are contained 0.4 mols of Zr (valency of +4), 0.4 mols of Ti (valency of +4), 0.1 mol of W (valency of +6) and 0.1 mol of Yb (valency of +3) per mol of the total amount of element species constituting the B-site, an average valency becomes 4 x 0.4 + 4 x 0.4 + 6 x 0.1 + 3 x 0.1 = 4.1.

It is desired that the above piezoelectric ceramic contains the constituent element species of the perovskite composite oxide in such amounts that satisfy the molar ratios expressed by the following formula,

$$[Pb_{y-a}M^1_a] \cdot [M^2_b M^3_c (Zr_{1-x}Ti_x)_{1-b-c}] \cdot O_{3+\alpha}$$

wherein M^1 is at least one kind of element species constituting the A-site selected from the group consisting of Ca, Sr, Ba, Nd and Li,

M^2 is at least one kind of element specifies constituting the B-site selected from the group consisting of Y, Dy, Ho, Er, Tm, Yb and Lu,

M^3 is at least one kind of element species constituting the B-site selected from the group consisting of W, Nb and Sb, and

a, b, c, x, y and α are expressed by the following conditions:

$0.98 \leqq y \leqq 1.01$

$0.01 \leqq a \leqq 0.1$

$0.005 \leqq b \leqq 0.025$

$0.005 \leqq c \leqq 0.015$

$0.45 \leqq x \leqq 0.55$

$-0.03 \leqq \alpha \leqq 0.02.$

It is desired that the piezoelectric ceramic has an average grain size in a range of 1 to 6 µm.

In the piezoelectric ceramic of the present invention, the average valency of the element species constituting the B-site in the perovskite composite oxide is set to lie in a particular range. Therefore, the piezoelectric ceramic exhibits a high Curie temperature and a high effective piezoelectric distortion constant, as well as excellent durability and reliability against high temperatures. Besides, the piezoelectric ceramic can be obtained through the filing at a low temperature (950 to 1000°C).

According to the present invention, further, there is provided a method of producing a piezoelectric ceramic comprising the steps of:

preparing a starting powder for a perovskite composite oxide which comprises a starting compound for the A-site and starting compounds for the B-site of the perovskite composite oxide, wherein at least a Pb oxide is contained as the starting compound for the A-site and at least a Zr oxide and a Ti oxide are contained as the starting compounds for the B-site, the starting compounds for the B-site being contained in such amounts that when the total amount of the element species constituting the B-site is calculated to be one mol, an average valency of the element species of the B-site is 4.002 to 4.009;

calcining the mixed powder at not higher than 900 °C;

preparing a slurry for molding by adding an organic binder to a calcined body obtained through the above step of calcining, and preparing a molded body of a predetermined shape by using the slurry; and

firing the molded body.

In this method of producing the piezoelectric

ceramic, it is desired that:

(1) The starting powder for the perovskite composite oxide has been adjusted to be a fine powder having an average grain size D_{50} of not larger than 0.8 μm;

(2) The calcined body has an average grain size D_{50} of not larger than 0.8 μm;

(3) Pb_3O_4 is used as the Pb oxide; and

(4) The firing is conducted at 950 to 1000°C.

In the production method of the present invention, the starting powder (mixed powder of a compound powder containing an element species constituting the A-site and a compound powder containing element species constituting the B-site) is so adjusted that an average valency of element species constituting the B-site lies in a predetermined range. Upon effecting the firing after calcined at a temperature as low as 900°C or lower, therefore, there is obtained a piezoelectric ceramic having high piezoelectric characteristics. Besides, even when the firing is effected at a low temperature (950 to 1000° C), the piezoelectric characteristics are not deteriorated.

According to the present invention, further, there is provided a laminated piezoelectric element obtained by alternately laminating piezoelectric layers and internal electrode layers, the piezoelectric layers being constituted by the piezoelectric ceramic.

That is, the laminated piezoelectric element has the piezoelectric layers that are formed by using the piezoelectric ceramic featuring excellent piezoelectric characteristics, and can be produced by co-firing the piezoelectric layers and the internal electrode layers having a high Ag ratio, offering a great advantage even from the standpoint of decreasing

the cost.

In the laminated piezoelectric element, further, the piezoelectric layers are subjected to the polarization treatment. Here, it is desired that the piezoelectric layers have been treated in an electric field in a no-load state prior to being subjected to the polarization treatment. Through the treatment in the electric field, gaps are partly formed in the interfaces among the piezoelectric layers and the internal electrode layers. Formation of the gaps helps increase the amount of displacement of the piezoelectric layers which are in contact with the internal electrode layers. As a result, it is made possible to very greatly increase the amount of displacement of the laminated piezoelectric element.

(Brief Description of the Drawings)

Fig. 1 is a schematic sectional view of a laminated piezoelectric element according to an embodiment of the present invention;

Fig. 2 is a view illustrating, on an enlarged scale, a major portion of the laminated piezoelectric element of Fig. 1;

Fig. 3 is a view illustrating an injection device using the laminated piezoelectric element of Fig. 1; and

Fig. 4 is a schematic sectional view of the laminated piezoelectric element according to another embodiment of the present invention.

(Best Mode for Carrying Out the Invention)

(Piezoelectric Ceramic)

The piezoelectric ceramic of the present invention comprises a perovskite composite oxide of an ABO_3 composition, and contains Pb as an element species that constitutes the A-site and contains Zr and Ti as element species that constitute the B-site. That is,

in the above piezoelectric ceramic, the peroviskite composite oxide particles represented by the following formula (1) are precipitated as main crystals,

$$(Pb, Q_A)(Zr, Ti, Q_B)O_3 \qquad --- (1)$$
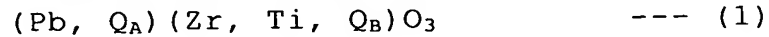
5   wherein Q_A is an element species constituting the A-site other than Pb,

Q_B is an element species constituting the B-site Other than Zr and Ti, and

Q_A and Q_B may not be present.

10   In the piezoelectric ceramic of the present invention, element species constituting the B-site of the perovskite composite oxide are contained in such amounts that an average valency thereof is in a range of 4.002 to 4.009 and, preferably, 4.003 to 4.007.

15   Therefore, the piezoelectric ceramic of the invention exhibits a high Curie temperature and a high effective piezoelectric distortion constant, as well as excellent durability and reliability against high temperatures. For example, when the average valency

20 of element species constituting the B-site lies outside the above range, the effective piezoelectric distortion constant drops and the Curie temperature decreases, too, when the piezoelectric ceramic is produced through the firing at a low temperature as

25 will be described later. Though it has not yet been clarified in the present invention why the above excellent characteristics are exhibited upon setting the average valency of element specifies constituting the B-site to lie in the above range, it is presumed

30 that the above element species contribute to forming the B-site even when the firing is conducted at a low temperature and there is formed an ideal perovskite composite oxide represented by the above formula.

From the standpoint of obtaining a piezoelectric

35 ceramic having a high Curie temperature and a high

effective piezoelectric distortion constant, further, it is desired that an average valency of the element species constituting the A-site is in a range of 1.99 to 2.01.

Under a condition where the average valency of element species constituting the B-site is within the above range, further, it is desired that the piezoelectric ceramic of the present invention contains the constituent element species of the perovskite composite oxide in such amounts that satisfy the molar ratios expressed by the following formula (2),
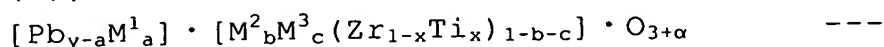
$$[Pb_{y-a}M^1_a] \cdot [M^2_b M^3_c (Zr_{1-x}Ti_x)_{1-b-c}] \cdot O_{3+\alpha} \qquad ---$$

(2)

wherein M^1 is at least one kind of element species constituting the A-site selected from the group consisting of Ca, Sr, Ba, Nd and Li,

M^2 is at least one kind of element specifies constituting the B-site selected from the group consisting of Y, Dy, Ho, Er, Tm, Yb and Lu,

M^3 is at least one kind of element species constituting the B-site selected from the group consisting of W, Nb and Sb, and

a, b, c, x, y and α are expressed by the following conditions:

$0.98 \leqq y \leqq 1.01$ and, particularly, $0.992 \leqq y \leqq 1.007$,

$0.01 \leqq a \leqq 0.1$ and, particularly, $0.03 \leqq a \leqq 0.08$,

$0.005 \leqq b \leqq 0.025$ and, particularly, $0.008 \leqq b \leqq 0.02$,

$0.005 \leqq c \leqq 0.015$ and, particularly, $0.006 \leqq c \leqq 0.009$,

$0.45 \leqq x \leqq 0.55$ and, particularly, $0.47 \leqq x \leqq 0.53$,

-0.03 $\leqq \alpha \leqq$ 0.02, particularly, -0.02 to 0.01 and,

most desirably, -0.01 to 0.005.

That is, upon partly substituting Pb in the A-site of the perovskite composite oxide with the element M^1 and upon partly substituting Zr and Ti in the B-site with elements M^2 and M^3, the Curie temperature and the effective piezoelectric distortion constant can be further enhanced to further improve the durability and reliability against high temperatures. From the standpoint of adjusting the average valency of the piezoelectric ceramic and increasing the Curie temperature and the effective piezoelectric distortion constant, it is desired to use at least one kind of Ca, Sr and Ba as the element M^1 (element constituting the A-site)and, more desirably, to use both Sr and Ba as the element M^1. In this case, an optimum element ratio of Sr and Ba is in a range of Sr:Ba = (1.5 to 2.5):(2.5 to 3.5). As the element M^2 (one element constituting the B-site), it is particularly desired to use Yb and as the element M^3 (another element constituting the B-site), it is particularly desired to use W.

Further, the parameters a, b, c, x, y and α representing the amounts of the above elements, most desirably, assume values within the above-mentioned ranges from the standpoint of adjusting the average valency of the piezoelectric ceramic, increasing the Curie temperature and the effective piezoelectric distortion constant and enhancing the durability against high temperatures.

Further, so far as the value of the parameter y representing the element ratio A/B of the element species of the A-site and the element species of the B-site lies within the above range, the Curie

temperature and the effective piezoelectric distortion constant can be very effectively increased, a drop in the output can be suppressed to be not larger than 10% in the durability testing at high temperatures of up to 10^9 cycles, and the firing can be realized at a low temperature. When, for example, the value y representing the ratio (A/B) is smaller than the above range, it becomes difficult to increase the density through the firing at a low temperature that will be described later. When the value y of (A/B) becomes greater than the above range, on the other hand, there tends to take place delamination.

It is further desired that the piezoelectric ceramic of the present invention has an average grain size of 1 to 6 µm and, particularly, 1.5 to 2.5 µm from the standpoint of enhancing the piezoelectric characteristics and improving the mechanical strength.

By setting the value of parameter α representing an excess amount of oxygen to lie within the above range as represented by the above formula (2), further, there is obtained an advantage of further highly stabilizing the piezoelectric characteristics and mechanical strength of the piezoelectric ceramic.

As described above, the piezoelectric ceramic of the present invention contains the perovskite composite oxide as a main crystal phase and, desirably, contains almost no different phase. The piezoelectric ceramic of the invention may inevitably contain Ag, Al, Fe, S, Cl, Eu, K, P, Cu, Mg and Si without, however, posing any problem from the standpoint of characteristics.

(Production of Piezoelectric Ceramic)

The above piezoelectric ceramic is produced by preparing a starting powder of a predetermined composition, calcining the starting powder, and

molding and firing the calcined body.

The starting powder is a mixture of a powder of the starting compound for the A-site and a powder of the starting compound for the B-site. As the starting compound for the A-site, there can be used a Pb oxide and, as required, an oxide or a carbonate of the above-mentioned element M^1. As the starting compound for the B-site, there can be used a Zr oxide (ZrO_2), a Ti oxide (TiO_2) and, as required, oxides or carbonates of the above-mentioned elements M^2 and M^3. Though there are various Pb oxides that can be used as the starting compound for the A-site, it is desired to use Pb_3O_4 from such a standpoint that it can be finely pulverized with ease, remains stable for a variety of solvents that will be described later, does not permit the composition thereof to vary, and can be easily adjusted for its composition. As described already, these starting compounds are so mixed that the average valency of element species constituting the B-site lies within the above-mentioned range and that the composition ratios of the formula (2) described above are satisfied.

It is further desired that the above starting powder is adjusted to be a fine powder having an average grain size D_{50} of not larger than 0.8 μm to be effectively fired at a low temperature of 1000°C or lower. The fine pulverization can be conducted by using, for example, a vibration mill, Atritor or a ball mill. In particular, it is desired to conduct the fine pulverization by wet-milling by using a ball mill containing, particularly, spherical balls of a diameter of not larger than 5 mm. As the material of the ball, it is desired to use zirconia since it is capable of suppressing impurities from mixing and of suppressing a decrease in the piezoelectric

characteristics even in case the impurities are mixed stemming from the balls.

The starting powder finely pulverized as described above is, as required, dried or dehydrated and is calcined in a low temperature region of not higher than 900°C, preferably, 700 to 800°C and, more preferably, 730 to 760°C. It is desired that the calcined body that is obtained is suitably milled and adjusted for its grain size so as to have a uniform grain size distribution of an average grain size D_{50} of not larger than 0.8 μm and, particularly, an integrated grain size D_{90} of not larger than 0.9 μm. It is desired that the BET specific surface area thereof is not smaller than 7 m^2/g and, particularly, not smaller than 8 m^2/g due to the milling. That is, as a result of finely pulverizing the starting powder, the calcined body needs be milled only slightly (milled to an extent of digesting the aggregate) to adjust the grain size and, hence, to maintain a high reactivity, making it possible to obtain the piezoelectric ceramic having the above-mentioned characteristics through the firing at a low temperature of 1000°C or lower. For example, when the calcined body is strongly milled as is usually done, excess of shock and heat are imparted to the powder of before being fired making it difficult to obtain the piezoelectric ceramic having the above-mentioned characteristics through the firing at 1000°C or lower.

Next, a powder of the calcined body of which the grain size is adjusted as described above is molded into a predetermined shape. The molding is conducted by using means known per se. For example, the calcined powder is mixed into an organic binder such as of an acrylic resin and is, as required, mixed with a solvent such as water or an alcohol and a

plasticizer to prepare a slurry for molding. By using molding means such as a doctor blade method or an extrusion-molding method, the slurry is molded into a predetermined shape.

5   After the binder is removed, the above molded body is fired to obtain a piezoelectric ceramic having the above-mentioned characteristics. The binder is removed by heating at a temperature of about 300 to about 400°C for about 5 to about 40 hours. In the

10   present invention, the firing may be conducted in a low temperature region of not higher than 1000°C and, particularly, at 950 to 1000°C for about 2 to 5 hours. Through the firing at such a low temperature, there is obtained a piezoelectric ceramic which is dense and

15   having excellent characteristics as described above.
(Laminated Piezoelectric Element)
    The above piezoelectric ceramic can be very effectively used, particularly, as an element for constituting the laminated piezoelectric element.

20   Fig. 1 is a view schematically illustrating the structure of the laminated piezoelectric element according to an embodiment, and Fig. 2 is a view illustrating, on an enlarged scale, a major portion thereof.

25   In Figs. 1 and 2, the laminated piezoelectric element has a laminate (element body) 5 obtained by alternately laminating a plurality of piezoelectric layers 1 and internal electrode layers 3. External electrode plates 7, 7 are connected to different side

30   surfaces of the element body 5, and lead wires 9 are connected to the external electrode plates 7 (i.e., one of the external electrode plates 7, 7 serves as a positive electrode and the other one serves as a negative electrode).

35   As will be understood from Fig. 2, further, the

neighboring internal electrode layers 3 are connected
to different external electrode plates 7. When a
predetermined voltage is applied to the external
electrode plates 7, 7, therefore, electric fields of
5 opposite directions are applied to the neighboring
piezoelectric layers 1, 1.

 In the laminated piezoelectric element, the
piezoelectric layers 1 are constituted by using the
piezoelectric ceramic of the invention described
10 above, each having a thickness in a range of 0.05 to
0.25 mm. In the piezoelectric layers 1, the ceramic
has an average grain size of, usually, in a range of 1
to 6 µm as described above. It is, however, desired
that the ceramic has an average grain size of not
15 smaller than 1.5 µm and, particularly, not smaller
than 2 µm from the standpoint of enhancing the
piezoelectric characteristics, and has an average
grain size of not larger than 4 µm and, particularly,
not larger than 3 µm from the standpoint of enhancing
20 the mechanical strength. The average grain size of
the ceramic will be controlled depending upon the
starting powder described above and upon the average
grain size of the calcined body.

 It is desired that the internal electrode layers
25 3 each have a thickness of 0.003 to 0.01 mm, and that
the numbers of the piezoelectric layers 1 and the
internal electrode layers 3 are each 100 to 400 to
obtain desired characteristics. Further, the
laminated piezoelectric element (element body 5) may
30 have any shape such as a square pole, a hexagonal pole
or a cylindrical pole but desirably has the shape of a
square pole from the standpoint of easy cutting.

 In the laminated piezoelectric element, the
internal electrode layers 3 may be formed by using
35 various metals, e.g., noble metals such as Ag, Pd or

Pt, or base metals such as Cu or Ni. From the
standpoint of maintaining a high electric conduction
and a low cost, however, it is particularly desired
that the content of Ag is not smaller than 85% by
mass, particularly, not smaller than 90% by mass and,
most desirably, not smaller than 95% by mass with
respect to the whole metals. The internal electrode
layers 3 containing Ag in large amounts can be fired
at a low temperature. The above-mentioned ceramic can
be formed by firing in a low temperature region of 950
to 1000°C. Therefore, the piezoelectric layers 1 and
the internal electrode layers 3 can be co-fired, which
is a great advantage of the invention.

When the internal electrode layers 3 contain Ag
in large amounts as described above, ionic migration
of Ag may easily occur at the time of firing. The
ionic migration, however, can be suppressed by
containing Pt in an amount of not smaller than 0.1% by
mass in the internal electrode layers 3. Further, the
ionic migration can be suppressed by using Ag and Pd
in combination. In this case, the Pd content is
desirably about 5 to 20% by mass.

The laminated piezoelectric element can be
produced in compliance with the above-mentioned method
of producing the piezoelectric ceramic.

That is, relying upon the method described above,
a slurry for molding is prepared by using the calcined
starting powder. By using this slurry, there is
prepared a green sheet for piezoelectric layers 1.

An electrically conducting paste prepared by
mixing the above conducting components such as Ag, Pd
or Pt and an organic binder or a solvent, is printed
onto one surface of the green sheet by a screen-
printing method to form a conducting pattern
corresponding to the internal electrode layers 3.

After the conducting pattern is dried, a plurality of green sheets forming the conducting patterns are laminated in a predetermined number of pieces. Thereafter, green sheets without electrically conducting paste are laminated on the uppermost layer and on the lowermost layer of the laminate to fabricate a pole-like laminate corresponding to the element body 5.

Next, the pole-like laminate is integrated by heating at 50 to 200°C under the application of a pressure, is cut into a predetermined size and, after the binder is removed, is fired at a low temperature (950 to 1000°C) to obtain a laminated sintered body that becomes the element body 5 as described above in connection with the method of producing the piezoelectric ceramic.

Ends of the internal electrode layers 2 are exposed on the side surfaces of the thus obtained element body (laminated sintered body) 5. Therefore, the ends of every other internal electrode layers 2 are ground in the predetermined two side surfaces of the element body 5 to form grooves. The grooves formed in one side surface and the grooves formed in the other side surface are alternate to each other. These grooves, usually, have a depth of about 50 to about 150 µm and have a width (length in the direction of lamination) of about 50 to about 100 µm.

The thus formed grooves are, as required, filled with an insulator such as a silicone rubber, and the external electrode plates are stuck to the side surfaces forming the grooves by using an adhesive or the like. Therefore, the one external electrode plate 7 and the other external electrode plate 7 are connected to the ends of different internal electrode layers 3 in an alternate manner.

Thereafter, lead wires 9 are connected to the external electrode plates 7, 7 to obtain a laminated piezoelectric element of a structure shown in Figs. 1 and 2. The laminated piezoelectric element is coated over the outer peripheral surfaces thereof with a silicone rubber by such a method as dipping, and is put to the polarization treatment by applying a polarizing electric field of 3 kV/mm, and is finally used as a piezoelectric actuator.

The above laminated piezoelectric element can be produced by co-firing the piezoelectric layers and the internal electrode layers having a high Ag ratio, and exhibits a high Curie temperature and a high effective piezoelectric distortion constant in compliance with the characteristics of the piezoelectric ceramic that constitutes the piezoelectric layers, and features excellent durability and reliability against high temperatures. The laminated piezoelectric element is useful as an injection device for media such as fuels and gases. The injection device contains the laminated piezoelectric element of the above-mentioned structure in a container that has, for example, an injection hole, and is equipped with a valve for injecting a liquid from the injection hole when the laminated piezoelectric element is driven.

A constitution of the above injection device is shown in Fig. 3, wherein a laminated piezoelectric element (piezoelectric actuator) 43 of the above-mentioned structure is contained in a cylinder 39 of a container 31.

An injection hole 33 is formed at an end of the container 31, and a needle valve 35 is contained in the container 31 to open and close the injection hole 33.

A fuel passage 37 is communicated with the

injection hole 33 in a manner to be interrupted by the needle valve 35. The fuel passage 37 is communicated with an external fuel supply, and a fuel is fed to the fuel passage 37 at all times maintaining a

5 predetermined high pressure. That is, when the needle valve 35 permits the injection hole 33 to be opened, the fuel supplied to the fuel passage 37 is injected into a combustion chamber (not shown) of an internal combustion engine with the predetermined high

10 pressure.

Further, an upper end of the needle valve 35 has a large diameter, is continuous to a piston 41 which can slide in the cylinder 39, and the piston 41 is urged upward by an initially coned disc spring 45 and

15 is coupled to the piezoelectric actuator 43 contained in the cylinder 39.

In this injection device, when the piezoelectric actuator 43 extends due to the application of a voltage, the piston 41 is pushed, the needle valve 35

20 closes the injection hole 33, and the supply of fuel is interrupted. When the application of voltage discontinues, further, the piezoelectric actuator 43 contracts, the initially coned disc spring 45 pushes the piston 41 back, and the injection hole 33 is

25 communicated with the fuel passage 37 permitting the fuel to be injected.

The injection device employs the above-mentioned laminated piezoelectric element of high performance fabricated at a low cost as the actuator which is the

30 heart of the device. Therefore, the present invention makes it possible to enhance performance of the injection device and to decrease its cost.

Further, the laminated piezoelectric element of the invention can be designed in a variety of ways.

35 For example, gaps can be locally formed in the

interfaces among the piezoelectric layers 1 and the internal electrode layers 3 to thereby greatly enhance the amount of displacement of the laminated piezoelectric element.

Fig. 4 illustrates the structure of the laminated piezoelectric element forming the above gaps. As shown in Fig. 4, the laminated piezoelectric element has a basic structure which is the same as that of the laminated piezoelectric element shown in Fig. 1 that was described above, but has partial gaps 11 in the interfaces among the piezoelectric layers 1 and the internal electrode layers 3.

That is, prior to the use, a voltage is applied across the external electrode plates 7, 7 and a polarizing electric field (3 kV/mm) is applied to the piezoelectric layers 1 to polarize the laminated piezoelectric element. The polarization treatment is usually conducted by locking the element body 5 in a direction in which it is to be compressed by applying a load. Therefore, the piezoelectric layers 1 are held in a state of being clamped by the internal electrode layers 3, and the junction strength is enhanced among the above layers. In the laminated piezoelectric element produced by co-firing, in particular, the piezoelectric layers 1 and the internal electrode layers 3 are tightly and intimately contacted together greatly enhancing the junction strength among the piezoelectric layers 1 and the internal electrode layers 3. However, as the junction strength increases among the piezoelectric layers 1 and the internal electrode layers 3, the piezoelectric layers 1 in contact with the internal electrode layers 3 are suppressed from displacing in the direction of surface thereof. As a result, the piezoelectric layers 1 are suppressed from displacing in the

direction of thickness thereof (direction of height of the element body 5), too, resulting in a decrease in the amount of displacement of the laminated piezoelectric element itself. In the embodiment of Fig. 4, however, clamping of the piezoelectric layers 1 by the internal electrode layers 3 is relaxed by the formation of gaps 11 suppressing an increase in the adhering strength among the layers. Therefore, the amount of displacement of the laminated piezoelectric element can be increased.

The above-mentioned gaps 11 can be formed through a suitable degree of treatment in an electric field under the application of no pressure prior to the above-mentioned polarization treatment. That is, the treatment in the electric field consists of suitably vibrating the piezoelectric layers 1 by applying an electric field of a suitable degree to the external electrode plates 7, 7 causing the surfaces of the internal electrode layers 3 to be partly separated away from the surfaces of the piezoelectric layers 1 and, at the same time, causing the surfaces of the internal electrode layers 3 to partly bite into dents in the surfaces of the piezoelectric layers 1. Therefore, gaps 11 of a suitable size are partly formed to decrease the junction strength by a suitable degree. The treatment in the electric field can be conducted by applying any one of a DC voltage, an AC voltage or a pulse voltage to the external electrode plates 7, 7. To lower the junction strength by a suitable degree while preventing the layers from exfoliating to a large extent, however, it is desired to apply the DC voltage. From the standpoint of lowering the junction strength by a suitable degree and maintaining a large electrostatic capacity of the piezoelectric layers 1, however, it is desired to

apply a voltage of not higher 200 V, preferably, not higher than 150 V but not lower than 50 V to maintain a suitable degree of junction strength. The time for treatment in the electric field may differ depending

5 upon the voltage that is applied but is, usually, not shorter than 30 seconds and, particularly, from about 10 to about 180 seconds. Further, when the treatment in the electric field is conducted by applying the AC voltage, the frequency thereof is, desirably, not

10 higher than 1 kHz. To effectively conduct the treatment in the electric field, further, it is desired that the treatment is conducted in an atmosphere of a relative humidity (RH) which is not lower than 40%.

15 To effectively lower the junction strength by the above treatment in the electric field, further, it is desired that the thickness of the internal electrode layers 3 is set to be not larger than 10 µm.

It is further desired that the electrically

20 conducting paste for forming the internal electrode layers 3 does not exhibit blending property to the green sheet that is forming the piezoelectric layers 1 from the standpoint of suppressing the junction strength. Concretely speaking, the solvent or the

25 binder used for the electrically conducting paste should be the one different from the solvent or the binder used for forming the green sheet. The poorer the affinity between them, the more the components constituting the piezoelectric layers 1 are suppressed

30 from infiltrating into the internal electrode layers 3 during the firing. Therefore, the spot-like cavities 13 tend to be formed in the internal electrode layers 3. As a result, the adhesion strength can be suppressed to be low among the piezoelectric layers 1

35 and the internal electrode layers 3 making it possible

to increase the amount of displacement of the laminated piezoelectric element.

In the present invention, the gaps 11 partly formed among the piezoelectric layers 1 and the

5 internal electrode layers 3 as described above, have a width t of not larger than 1 μm in the direction of thickness. In particular, the gaps 11 having a small thickness t can be confirmed by observing the interfaces of the layers by using a microscope.

10 In the thus laminated piezoelectric element, it is desired that the number of the laminated layers (total number of the piezoelectric layers 1 and the internal electrode layers 3) is not smaller than 100 from the standpoint of increasing the amount of

15 displacement. From the standpoint of reducing the weight, further, it is desired that each piezoelectric layer 1 has a thickness of not larger than 300 μm and, particularly, not larger than 100 μm.

The above laminated piezoelectric element is

20 useful as a laminated piezoelectric actuator, as well as for such applications as a laminated piezoelectric transformer, a laminated capacitor and the like.
(EXAMPLES)

The invention will now be described by way of the

25 following Experiments.
(Experiment 1)

Starting powders for piezoelectric ceramics were prepared by weighing the powders of Pb_3O_4, ZrO_2, TiO_2, $BaCO_3$, $SrCO_3$, WO_3 and Yb_2O_3 of high purities in

30 predetermined amounts, and wet-mixing the powders in a ball mill having zirconia balls of a diameter of 5 mm for 20 hours. In the starting powders, $BaCO_3$ and $SrCO_3$ were used at a mol ratio of 3:2 as the element M^1 of the A-site in the following formula (1),

35 $$[Pb_{y-a}M^1_a] \cdot [M^2_b M^3_c (Zr_{1-x}Ti_x)_{1-b-c}] \cdot O_{3+\alpha} \qquad --- \quad (1)$$
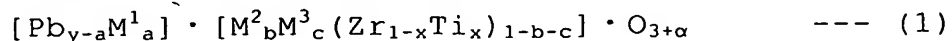
and a was selected to be 0.05. As the element M^2 and element M^3 of the B-site, there were used WO_3 and Yb_2O_3, respectively, and average valencies of the B-site were set to be as shown in Table 1. In this Experiment,

5 the average valency of the A-site was set to be 2, and the ratio A/B was set to be 1.

The above starting powders were dehydrated, dried, calcined at 750°C for 3 hours, and were pulverized to adjust average grain sizes (D_{50}) of the

10 calcined bodies to be not larger than 0.8 μm and BET specific surface areas to be not smaller than 8 m^2/g. There was obtained calcined powders for producing the piezoelectric ceramics and the laminated piezoelectric elements of the present invention.

15 First, to evaluate the densities of the piezoelectric ceramics only, molded bodies having a diameter of 10 mm and a thickness of 1 mm were prepared by using the above calcined powders and were fired at 1000°C (the slurries used for forming the

20 molded bodies possessed the same compositions as those used for forming the actuators that will be described below). The piezoelectric ceramics were measured for their densities and grain sizes. The samples having relative densities of not higher than 95% were

25 regarded to be of low densities and to be defective. The ceramic samples having polished cross sections were measured for their grain sizes by using an electron microscope.

Further, the above calcined powders, an acrylic

30 resin binder and a plasticizer (dibutyl phthalate: DBP) were mixed together to prepare slurries from which ceramic green sheets of a thickness of 150 μm were prepared by a slip-casting method. A conducting paste comprising Ag-Pd as a chief component and having

35 an Ag/Pd ratio as shown in Table 1 was printed onto

the surfaces on one side of the green sheets maintaining a thickness of 5 μm by a screen-printing method, and was dried. Two hundred pieces of the green sheets were laminated, and 10 pieces of green sheets without coated with the conducting paste were laminated on both the upper end and the lower end of the laminates.

Next, the laminates were integrated by the application of a pressure while being heated at 100°C. The laminates were cut into a size of 12 mm x 12 mm and, thereafter, the binder was removed therefrom at 800°C for 10 hours, and were fired at 950 to 1000°C for 2 hours to obtain laminated sintered bodies that could be used as the actuator bodies.

External electrode plates (positive electrode plate and negative electrode plate) were formed on the two side surfaces of the laminated sintered bodies so as to alternately meet the ends of the internal electrodes included in the piezoelectric ceramics along the two side surfaces. Thereafter, the lead wires were connected to the positive electrode plate and to the negative electrode plate, and the outer peripheral surfaces were coated with a silicone rubber by dipping followed by the application of a polarizing voltage of 3 kV/mm to effect the polarization treatment thereby to obtain laminated piezoelectric elements.

The thus obtained laminated piezoelectric elements were evaluated for their effective piezoelectric distortion constants, Curie temperatures and durability against high temperatures.

The effective piezoelectric distortion was evaluated by applying a voltage of 0 to 200 V in a state where pre-load of 150 kgf has been applied in a direction of lamination to the samples fixed onto a

vibration-proof plate, measuring the amounts of change in the overall length of the samples, and dividing the amounts of change by the number of the laminated layers and by the applied voltage.

5   The Curie temperatures were found by measuring the temperature characteristics of electrostatic capacities of the piezoelectric ceramics.

      The durability testings against high temperatures were evaluated by repetitively driving the samples up

10   to 10^9 times in a constant-temperature vessel under the conditions of a temperature of 150°C and a frequency of 50 Hz being applied with a load of 150 kgf.

      For comparison, the samples (Nos. 1, 7) having average valencies of the B-site lying outside the

15   range of the present invention were similarly evaluated.

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Table 1

Sample No.	Average valency of B-site	Amount of M^2 (mol) b	Amount of M^3 (mol) c	Ti/(Zr+Ti) ratio X	Ag/Pd	Effective piezoelectric distortion consyants d_{33} pm/V	Curie temp. (°C)	Durability to hi-temp. 10^9 cycles
*1	3.994	0.010	0.0020	0.475	95/5	690	335	○
2	4.002	0.010	0.0060	0.485	95/5	860	331	○
3	4.004	0.010	0.0070	0.485	95/5	865	330	◎
4	4.005	0.010	0.0075	0.480	95/5	930	328	◎
5	4.006	0.010	0.0080	0.485	95/5	868	328	◎
6	4.008	0.010	0.0090	0.490	95/5	870	325	○
*7	4.014	0.010	0.0120	0.495	95/5	630	320	○
8	4.002	0.010	0.0060	0.485	90/10	889	331	○
9	4.004	0.010	0.0070	0.485	90/10	894	331	◎
10	4.005	0.010	0.0075	0.480	90/10	961	329	◎
11	4.006	0.010	0.0080	0.485	90/10	897	328	◎
12	4.008	0.010	0.0090	0.490	90/10	899	326	○
13	4.002	0.010	0.0060	0.485	85/15	908	331	○
14	4.004	0.010	0.0070	0.485	85/15	913	330	◎
15	4.005	0.010	0.0075	0.480	85/15	982	328	◎
16	4.006	0.010	0.0080	0.485	85/15	916	329	◎
17	4.008	0.010	0.0090	0.490	85/15	918	326	○

Marks * represent samples lying outside the scope of the present invention.

** ◎ represents a drop of not larger than 10% in the amount of displacement after 10^9 cycles.

From the results of Table 1, the samples Nos. 2 to 6 and 8 to 17 which were the laminated piezoelectric elements of the invention all possessed relative densities of ceramics of not smaller than 95% and average grain sizes of 1 to 6 µm. These samples, further, exhibited the Curie temperatures of not lower than 325°C, effective piezoelectric constants of not smaller than 860 pm/V, and none of them were regarded to be defective in the testing of durability against high temperatures, i.e., in the operation testing of up to 10^9 cycles.

In particular, the samples Nos. 3 to 5, 9 to 11, and 14 to 16 having an average grain size of piezoelectric ceramics of 2 µm exhibited Curie temperatures of not lower than 328°C, effective piezoelectric distortion constants of not smaller than 865 pm/V and drops in the amount of displacement of not larger than 10% in the durability testing against high temperatures of up to 10^9 cycles.

On the other hand, the samples Nos. 1 and 7 lying outside the scope of the invention exhibited low effective piezoelectric distortion constants and drops in the amount of displacement of not smaller than 10% in the durability testing against high temperatures.
(Experiment 2)

As the starting powder, first, there was used a calcined powder of the composition same as the sample No. 3 of Experiment 1.

The calcined powder, an organic binder (polyvinyl butyral) and a plasticizer (DBP) were mixed together to prepare a slurry from which a ceramic green sheet of a thickness of 100 µm was prepared by the slip-casting method. The ceramic green sheet was cut into a desired size, and a conducting paste was printed onto one surface thereof by the screen-printing method

such that the thickness thereof was 5 µm and the effective area of the electron pattern was 90% that of the ceramic green sheet after it has been cut.

The conducting paste was prepared by adding an organic binder (ethyl cellulose) and a plasticizer to a mixed powder of Ag/Pd = 95/5 (% by mass). For some samples, the starting powder for the piezoelectric ceramic used for forming the green sheet was mixed in an amount of 3% by weight as a base material.

Next, the conducting pattern was dried, and 200 pieces of the green sheets on which the conducting pattern has been formed were laminated, and 10 pieces of green sheets without coated with the conducting paste were laminated on both the upper end and the lower end of the laminate.

Next, the laminate was pressed while being heated at 100°C to obtain a laminated sintered body that could be used as the actuator body in quite the same manner as in Experiment 1. External electrode plates and lead wires were connected thereto, and the outer peripheral surfaces were coated with a silicone rubber by dipping to obtain a laminated piezoelectric element.

The thickness of piezoelectric layers of the thus obtained laminated piezoelectric element was 80 µm on an average, and the thickness of the internal electrode layers was 2.5 µm on an average. The whole thickness was 25 mm.

The piezoelectric element was treated in an electric field shown in Table 2 at a humidity of 50%RH and was, then, subjected to the polarization treatment by applying a polarizing voltage of 3 kV/mm. Here, however, the sample No. 1 was not treated in the electric field. In the samples treated in the electric field, the internal electrode layers were

partly biting into the recessed portions of the piezoelectric layers as observed by using an electron microscope.

The laminated piezoelectric elements fabricated as described above were evaluated for their changes in the electrostatic capacity when an electric field was applied thereto and for their amounts of displacement relying on the methods described below. The results were as shown in Table 2. Each testing was conducted by using the samples in a number of 50.

Changes in the electrostatic capacity were measured by using an impedance analyzer under the conditions of a frequency of 1 kHz and 1 V.

The amounts of displacement were measured by applying a DC voltage of 200 V for 60 seconds.

Further, the piezoelectric elements were cut in a vertical direction, and the cut surfaces were observed by using a microscope (magnification of 200 times) to judge the presence of partial gaps (opening portions) among the internal electrode layers and the piezoelectric layers. The results were as shown in Table 2 (gaps of not larger than 1 μm were observed in the samples that were treated in the electric field).

Table 2

Sample No.	Conducting paste contains material	Treated in electric field	Kind of electric field	Voltage (V)	Time (sec)	Gap	Change in capacity (%)	Amount of displacement (μm)
*1	yes	no	-	-	-	no	0	25
2	yes	yes	DC	100	100	yes	90	40
3	yes	yes	DC	50	100	yes	97	40
4	yes	yes	DC	150	100	yes	82	37
5	yes	yes	DC	100	300	yes	88	39
6	yes	yes	AC**	100	100	yes	82	30
7	yes	yes	pulse ***	100	100	yes	80	30
8	yes	yes	DC	200	100	yes	75	35
9	no	yes	DC	100	100	yes	90	37

A mark * represents a sample lying outside the scope of the present invention.

A mark ** represents a frequency of 1 Hz.

A mark *** represents a duty of 0.5 sec/0.5 sec.

From the results of Table 2, the sample No. 1 that was subjected to the polarization treatment without being treated in the electric field exhibited the amount of displacement of 25 µm. On the other hand, the samples Nos. 2 to 9 that were subjected to the polarization treatment after having been treated in the predetermined electric field exhibited the amounts of displacement of not smaller than 30 µm. In particular, the samples Nos. 2 to 5, 8 and 9 that were treated in an electric field by the application of a DC voltage of 50 to 150 V exhibited the amounts of displacement of not smaller than 35 µm.